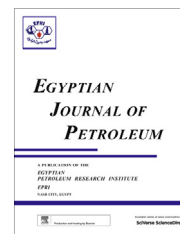




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FULL LENGTH ARTICLE

# Comparison between fixed and fluidized bed cathodes and effect of supporting electrolyte in electrochemical removal of copper ion from dilute solutions



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## KEYWORDS

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**Abstract** Comparison between fixed and fluidized bed cathodes was experimentally investigated in a circulated-batch system. The cell was made of a Perspex column of cylindrical shape; the inside diameter and the height were 10 and 70 cm, respectively. The results indicated that the performance of the fixed bed is better than that of fluidized bed considering the rate of removal percent and current efficiency.

Experimental study of the role of the supporting electrolyte in electrolytic cells confirmed that, type and concentration of supporting electrolyte have a remarkable effect on the two aforementioned parameters as well as the rate of removal. Using of NaCl showed better results than Na<sub>2</sub>SO<sub>4</sub>.

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## 1. Introduction

Heavy metals are classified as toxic metals. These metals cause environmental pollution (heavy-metal pollution). This sort of pollution can arise from many sources such as purification of

metals, preparation of nuclear fuels, metal finishing, mining waste, fertilizer manufacturing, petroleum refining and electroplating industries. Also some products such as paints, pigments, steel works and electrical equipments are sources of heavy metal contamination [1]. Electroplating is the primary source of cadmium, chromium and copper. Copper is an essential trace nutrient to all high plant and animal life. In animals, including humans, it is found primarily in the blood stream, as a co-factor in various enzymes and in copper-based pigments. However, sufficient amounts of copper can be poisonous and even fatal to organisms [2].

Various methods have been proposed to remove heavy metal ions from wastewater using, as representative examples,

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adsorption, electrodialysis, chemical precipitation, membrane filtration, biosorption, electrochemical methods, and ion-exchange resin [3]. Each of these methods has its own advantages and disadvantages [4]. The use of electrochemical approach to recover metal ions in the wastewater in their metallic state can be considered as a relatively simple and clean method. The electrochemical technique is one-step process for both jobs, i.e. it does not only diminish the heavy metal concentration to the safe level but also it allows recovery of precious metals such as Cu, Ag and Au.

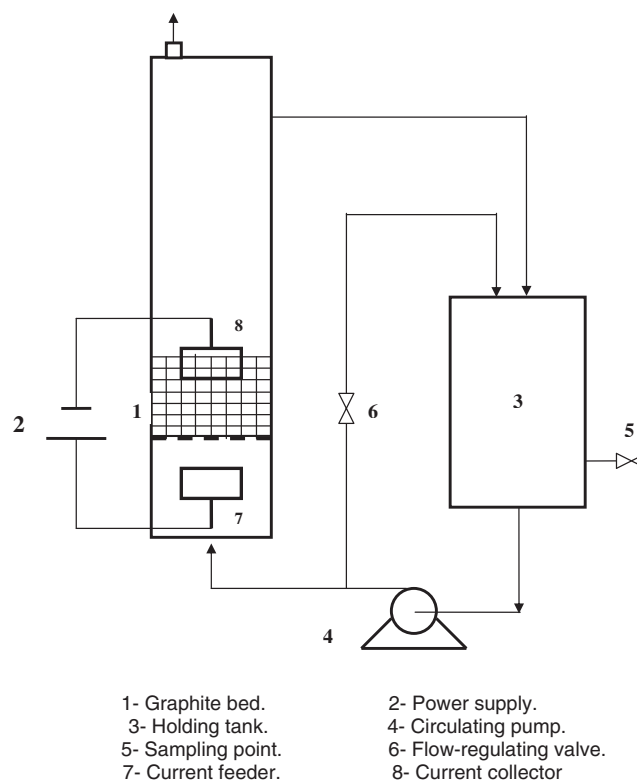
For metal electrodeposition from dilute solutions, the plain electrode was inadequate because of poor mass transfer rate. The process for the removal and/or the recovery of copper requires, beside some other operational factors, electrodes of large surface area and hydrodynamic region that secure high mass transfer rates. Packed-bed electrodes can realize these two factors [5]. So, as discussed by Bennion et al. [6] the potential difference between the carbon matrix and the solution at all points within the porous electrode should be sufficient, but not too large to ensure copper deposition without hydrogen evolution.

### 1.1. Packed bed electrode

A fixed bed electrode is a three-dimensional porous one. The cell is used in closed water recycling systems in the electroplating industry, mining, mineral processing and metallurgical industries. The cell offers particularly high values of electroactive area per unit reactor volume ( $A_s$ ), improved productivity, energy efficiency in electrosynthesis applications, has the ability to remove metal ions from aqueous solutions to very low levels and capability of providing high fractional conversion (sufficiently large residence time). While it may suffer from non-uniform potential distribution within the electrode matrix will lead to low current efficiency and poor selectivity. The other type is fluidized bed electrode, fluidized bed electrode operates at high electrolyte flow, when the upward electrolyte flow through an unrestrained particulate bed is sufficiently high, fluidization of the electrode particles may occur and the electrode-electrolyte combination behaving like a single fluid. It gives a very large surface area to volume ratio so for any given cell, the current density at the cathode surface is very low, high mass transport rate which combines high conversion and space time yield, continuous extraction of metals from industrial process liquors and the electrical and physical contact between particles may help to provide an active electrode surface. However, in practice, control of the fluidization can be a problem due to non-uniform reactor geometry, particle agglomeration, unwanted metal-deposition on the feeder electrode, separator damage due to erosion or electrical shorting caused by metal particles lodging near the membrane and the potential distribution can be complex which is affected by the shape and dimensions of the bed, positioning of the feeder and counter electrode(s), the degree of bed expansion, electrolyte composition and gas evolution [7]. Moreover, problems with the electrochemical treatment of some wastewaters from the plating industry, for instance, are the low concentration of the electroactive species and the conductivity due to a lack of supporting electrolyte and a high pH. The use of designs with high surface area

electrodes or enhanced mass transfer may improve the process. The current needed for the removal of metal ions is low and, because the energy consumption is not critical, low current efficiencies may be acceptable. A major drawback of a three-dimensional electrode in a poor conducting solution is the excessive ohmic potential drop in the solution, so that the electrode reaction penetrates the electrode matrix poorly. This condition becomes more critical for solutions with a very little supporting electrolyte. Operation with a three-dimensional electrode requires the careful selection of the electrolytic conditions [8]. Typically, a supporting electrolyte, such as an acid or a base, or occasionally a conducting salt, is added to the electrolytic solution to provide high ionic conductivity. The supporting electrolyte does not participate in the electrode reactions, but is, intentionally, required to reduce the resistivity within the electrolyte. The higher resistivity that otherwise occurs being the cause of the non-uniformity in the current density. Even the addition of a small amount, e.g., 0.2 M, of an acid or a base will typically increase the electrolyte conductivity quite significantly (e.g., double the conductivity) [9].

The addition of NaCl would also lead to decrease in power consumption because of the increase in conductivity. Moreover, the electrochemically generated chlorine was found to be effective in water disinfections [10]. The aim of this work is to study the effects of cell type and the role of supporting electrolyte on removal percent and current efficiency of the processes.



**Figure 1** Adopted system for copper removal. 1. Graphite bed. 2. Power supply. 3. Holding tank. 4. Circulating pump. 5. Sampling point. 6. Flow-regulating valve. 7. Current feeder. 8. Current collector.

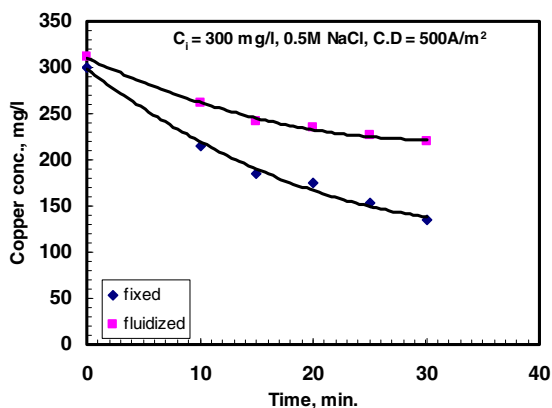
## 2. Experimental technique

### 2.1. Experimental set-up

A schematic representation of the experimental set-up is shown in Fig. 1. The set-up consisted of an electrolytic cell, D.C. power supply, holding tank, flow-regulating valve and circulation pump. The cell was made of a Perspex column of cylindrical shape; the inside diameter and the height were 10 and 70 cm, respectively. The column is separated by a flow distributor into upper and lower parts. The current feeder (anode) was fixed in the lower part of the column while the current collector (cathode) was in the upper part. Both feeder and collector were made of 304-type stainless steel (304 SS). The feeder had a cup shape, opened at one side and closed at the other. The cathode is disk like collector with several legs to give good contact with the particulate-bed.

### 2.2. Materials and methods

The chemicals were of analar grade. A regulated D.C. power supply type (Lodestar 8203) was used to supply power. A pH meter (type HI 8417 made by HANNA instruments) was used to measure the pH of the electrolyte. Electrolyte feed pump was (Corrosion-resistant magnetic – driven centrifugal pump, 220 V AC, 50 HZ, 90 W) Ascoll, Italy. The copper concentration was measured by atomic absorption spectrophotometer PerkinElmer 1100 B. The flow rate, measured by graduated cylinder and stop watch, was fixed at  $750 \pm 50$  ml/min. The used electrolyte had an initial copper concentration in the range of 100–350 mg/l. Sodium chloride was used as a supporting electrolyte, the concentration of which was fixed at 0.5 M. At the start of each run the electrolyte was adjusted at pH = 3 by using either hydrochloric acid or sodium hydroxide. Samples were taken from the circulated solution each 5 min except for the first sample which was taken after 10 min. The current density was changed in the range from 100 to 500 A/m<sup>2</sup>. Experiments were carried out at room temperature ( $26^\circ\text{C} \pm 3$ ).



**Figure 2** Effect of cell type (fixed & fluidized bed cell) on the rate of copper removal at different electrolysis durations.

## 3. Results and discussion

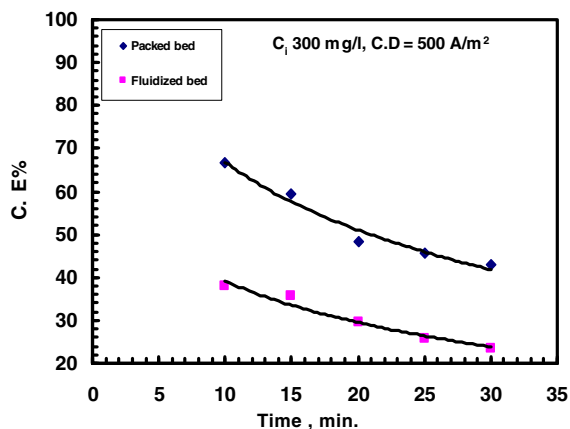
### 3.1. Comparison of fixed and fluidized bed cathodes

#### 3.1.1. Effect of cell type on the removal of copper

Fig. 2 illustrates copper concentration decrease versus electrolysis time for fixed and fluidized bed cells. The electrolyte composition was 300 mg/l copper ion concentration, 0.5 M NaCl as a supporting electrolyte and 500 A/m<sup>2</sup> current density. For fixed bed cell the solution flow rate was 0.8 l/min and the static bed length was 6.5 cm. While, on using this cell in the fluidized mode (i.e. as a fluidized bed cell), the flow rate increased to 4.5 l/min and due to the bed expansion the bed length changed to  $9.7 \text{ cm} \pm 2$ . From this figure it is clear that the removal of copper by using fixed bed cell is higher than that in the fluidized state, since the concentration of copper solution was decreased to 134.2 mg/l (removal percent (R.E %) = 55.3) after 30 min of electrolysis. While, using this cell as a fluidized bed and after 30 min of electrolysis, the final copper concentration reached to 219.8 mg/l (i.e. R.E % = 29.3 only). These results may be due to the non-uniformity of current and potential distributions within the fluidized bed cathode. Bed expansion may result in less contact between some of graphite particles leading to an increase in the cell resistance and then decreased the mass of copper removed. This problem did not exist in case of fixed bed cell. Moreover, the effective resistance of the particle phase in the fluidized bed cell was found to be three–four times larger than that of the fixed bed cell which may exhibit a relatively large polarization of graphite particles in the fluidized bed state and helps in the anodic dissolution of deposited copper (side reaction) Y. Matsuno et al. [11]. Similar results were reported by G. Chen [12] and DZ. E. Hadzismajlovic et al. [13].

#### 3.1.2. Current efficiency

Fig. 3 illustrates the current efficiency versus time of electrolysis for fluidized and fixed bed electrodes. The initial copper ion concentration was fixed at 300 mg/l, 0.5 M NaCl as a supporting electrolyte and 500 A/m<sup>2</sup> current density. As shown in this figure, the current efficiency decreased with increasing electrolysis time for both cells (fluidized and fixed bed cells). The current efficiency decreased with longer electrolysis time due to



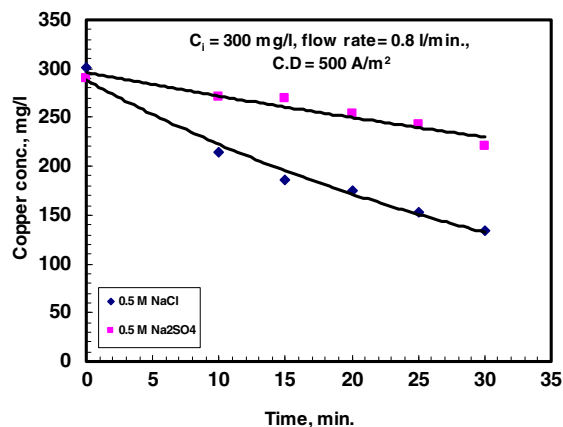
**Figure 3** Current efficiency versus time of electrolysis at packed and fluidized bed cell.

the decrease in copper concentrations through the deposition process. Then, limiting current value decreased which enhanced the hydrogen reduction side reaction. It is clear from this figure that, on using fixed bed cell, the higher current efficiency value is obtained. After 10 min of electrolysis current efficiency reached to 66.7, while, in case of fluidized bed cell, current efficiency fell to 37.9. Generally the fluidized bed system exhibits several technical problems such as metal deposition on the feeder electrode and existence of anodic or pseudo-anodic parts in the fluidized bed due to non-uniform potential distribution. This drawback causes poor current efficiency as discussed by Sarfarazi et al. [14]. As previously mentioned, the cell resistance within the fluidization state is higher than that in the case of fixed bed cell. Then, the potential drop increased i.e., hydrogen reduction side reaction, took place which decreased the current efficiency value.

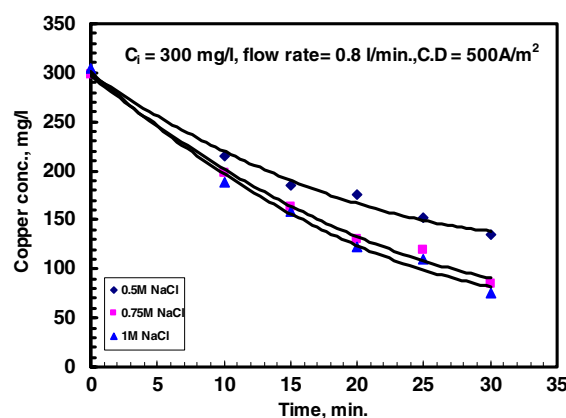
### 3.2. Type of supporting electrolyte

#### 3.2.1. Effect of supporting electrolyte on rate of deposition

Fig. 4 illustrates the decrease in the copper concentration during the deposition process versus electrolysis time for two types of supporting electrolyte (NaCl and  $\text{Na}_2\text{SO}_4$ ). The two electrolytes had constant a concentration of 0.5 M. Other conditions were fixed at the same condition 300 mg/l initial copper ion concentration, solution flow rate 0.8 l/min and 500 A/m<sup>2</sup> current density. Fig. 4 shows that the decrease of copper concentration is exponential in time in both electrolytes. In case of sodium chloride electrolyte and after 30 min the outlet copper concentration reached to 134.2 mg/l (i.e. R.E % = 55.3). However, in the utilization of sodium sulfate as supporting electrolyte, the final copper solution concentration reached to 221 mg/l (i.e. R.E % = 23.7). From these data, it is clear that, the usage of NaCl increased the conductivity of copper solution which catalyzed copper deposition reaction; this is reported by C. Ponce De Leon et al. [15]. Also, it was found that chloride ions could significantly reduce the thickness of the insulating layer formed at the electrode surface. Since these ions could reduce precipitation of other salts that exist in water or wastewater (e.g.  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ ) which increased the thickness of the insulating layer and hence increased the resistance. This was illustrated by G. Chen [12].

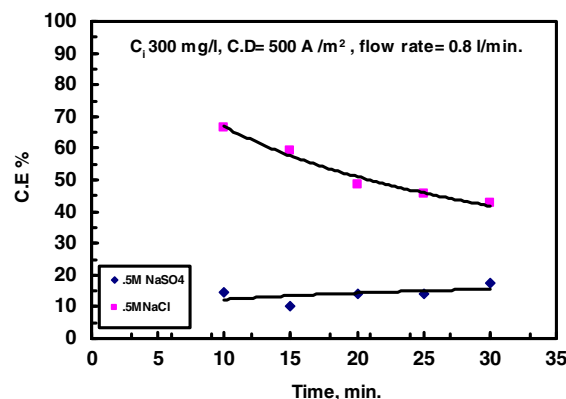


**Figure 4** Effect of type of supporting electrolyte on rate of removal of copper ions.

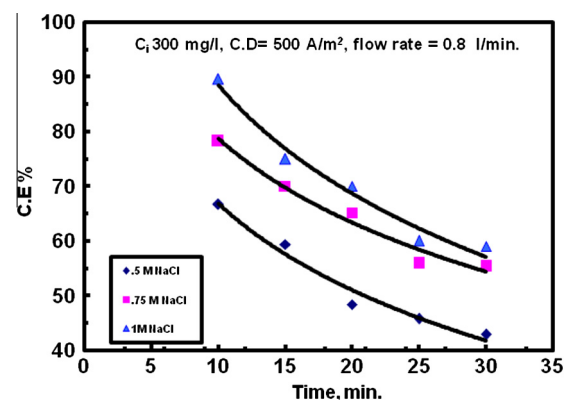


**Figure 5** Rate of copper removal versus time of electrolysis at different sodium chloride concentrations.

Fig. 5 shows the effect of sodium chloride concentration on the rate of removal of copper. Similar fixed conditions (300 mg/l copper ion concentration, 0.8 l/min flow rate and 500 A/m<sup>2</sup> current density) were applied. Sodium chloride concentration varied in the range of 0.5–1 M. From this figure, it is clear that the residual copper solution concentration decreases dramatically with electrolysis time and the addition of 1 M NaCl gives the higher rate of removal of copper. After 30 min, the final copper concentration reached 75 mg/l



**Figure 6** Current efficiency versus time of electrolysis at different supporting electrolytes.



**Figure 7** Current efficiency versus time of electrolysis at different sodium chloride concentrations.

**Table 1** Descriptive effect of operating variables on cell performance.

Operating variables							
Performance parameter	Cell type (fixed & fluidized bed cell)		Type of supporting electrolyte		NaCl concentration		
	Fixed bed cell	Fluidized bed cell	NaCl	Na <sub>2</sub> SO <sub>4</sub>	0.5 M	0.75 M	1 M
Rate of copper removal (R.E %) at different electrolysis time	55.3	29.3	55.3	23.7	55.3	71.6	75.3
Current efficiency (C.E %) at different electrolysis time	66.7	37.9	66.7	14.7	66.7	78.2	89.6

(i.e. R.E % = 75.3). Also, 0.75 M NaCl was used and after 30 min, the outlet copper concentration was 84.8 mg/l (i.e. R.E % = 71.6). From these data, it is clear that sodium chloride concentration of 0.75 and 1 M gave nearly the same results. However, the addition of 0.5 M NaCl and electrolysis for the same duration decreased the copper concentration to 134.2 mg/l only (i.e. R.E % = 55.3). This was previously discussed as the addition of chloride ions increases solution conductivity and could catalyze the copper deposition reaction. Therefore, it is better to use 1 M NaCl to obtain higher removal percent values.

### 3.2.2. Current efficiency

Fig. 6 shows how the current efficiency is affected by the supporting electrolytes (NaCl and Na<sub>2</sub>SO<sub>4</sub>). The molarity of both substances was the same at 0.5 M. The experimental conditions were fixed at 300 mg/l copper ion concentration, 0.8 l/min flow rate and 500 A/m<sup>2</sup> current density. These data indicated that, current efficiency decreased with electrolysis time in the presence of sodium chloride, while in addition of sodium sulfate current efficiency was nearly constant. This was explained as chloride ions could reduce the thickness of insulating layer formed at the electrode surface and hence decreased the potential between the electrodes (anode and cathode). Then, it resulted in decrease in cell power consumption which led to increase of current efficiency value G. chen [12]. After 10 min of electrolysis, current efficiency reached to 66.7% and then decreased with time due to the decrease of the copper concentration during the deposition process and side reactions contributions (hydrogen reduction reaction and anodic dissolution). In this work, the addition of sodium sulfate as a supporting electrolyte was insignificant because with the use of 0.5 M Na<sub>2</sub>SO<sub>4</sub> current efficiency fell to 14.7%. This may be explained as, generally, dilute solutions suffer from the lack of solution conductivity and sulfate anions which are bulky groups have a lower mobility value than chloride anions. So, it is recommended to use sodium chloride in order to obtain a higher current efficiency value. The obtained results agreed with the results of C. Ponce De Leon et al. [15] and G. Chen [12].

Current efficiency as function of sodium chloride concentration versus electrolysis time is represented in Fig. 7. The initial copper solution concentration was fixed at 300 mg/l, 500 A/m<sup>2</sup> current density and 0.8 l/min flow rate. Sodium chloride concentration varies from 0.5 to 1 M. From these results, it is clear that the current efficiency is dramatically decreased with electrolysis time. From visual inspection of these data, it is clear that, using 1 M NaCl and 0.75 M NaCl gave higher

current efficiency values than that obtained at 0.5 M NaCl. For instance, after 10 min of electrolysis current efficiency was 89.6% when the concentration of NaCl was 1 M while it dropped to 66.7% with decrease in the concentration of NaCl to 0.5 M. Hence, as previously mentioned, the addition of sodium chloride electrolyte gave a high current efficiency value and under the same experimental conditions, addition of 1 M NaCl led to the highest current efficiency. The obtained data are listed in Table 1.

## 4. Conclusion

- (1) The results indicated that the performance of fixed bed is better than that of fluidized bed from the points of view of removal percent and current efficiency.
- (2) Type and concentration of supporting electrolyte have a remarkable effect on the removal percent and current efficiency. Using of NaCl lead to better results than the utilization of Na<sub>2</sub>SO<sub>4</sub>.

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